

**CO₂ SELECTIVE CERAMIC MEMBRANE FOR WATER-GAS SHIFT REACTION WITH
CONCOMITANT FOR THE RECOVERY OF CO₂**

Quarterly Report for the Period January 2001- March 2001

**Paul K. T. Liu
Project Director**

MEDIA AND PROCESS TECHNOLOGY, INC.

April 9, 2001

**PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY
Under Cooperative Agreement
No. DE-FC26-00NT40922**

1. In-situ Crystallization for Hydrotalcite Membrane Synthesis

Rationale/Justifications

1. The study in the previous quarterly report suggested the possibility that hydrotalcite crystals in the neighborhood of $0.2\mu\text{m}$ or greater are immediately formed when the two solutions are combined together. The conventional approach (such as methods developed for the zeolitic membrane) involving the deposition of pre-formed crystals as seeds for crystal growth within the porous structure of the membrane becomes unnecessary. It is feasible to form a single crystal of hydrotalcite within the membrane porous structure if the two reactants (i.e., Na_2CO_3 and $\text{AlCl}_3/\text{MgCl}_2$) can be combined together within the porous structure. This rationale represents a major breakthrough, which can eliminate many tedious steps in the crystal formation as in the zeolitic membrane development.
2. A two-phase contactor using the membrane as an interphase appears to be an ideal device for us to achieve immediate crystal formation within the porous structure of the membrane. To demonstrate feasibility, a batch type two phase contactor was used to simplify the equipment design, acquisition and set-up.

Experimental

1. As an initial attempt, we filled the tube side of a membrane plugged at one end with one of the reactants, $\text{AlCl}_3/\text{MgCl}_2$, thereby completely wetting the pores of the substrate with the reactant. Then, the tube was dipped into a batch of well-mixed Na_2CO_3 solution. This approach was anticipated to embed hydrotalcite crystals in the pores of the support near the outer tubular surface, because the two solutions in contact at the membrane surface are stagnant and hence do not intermix rapidly.
2. Two membranes with 500\AA and $0.2\mu\text{m}$ pore sizes were selected as candidate substrates for this study. These $\alpha\text{-Al}_2\text{O}_3$ -based membranes are ideal for this application due to their chemical resistance to the high pH of the Na_2CO_3 solution (11 to 12). Each tubular membrane was 10" long, 5.5mm OD and 3.5mm ID with one end plugged with epoxy to hold the $\text{AlCl}_3/\text{MgCl}_2$ solution.
3. The tube was left in the batch solution for 0.5 to 1 hour to assure complete crystal formation. Then the tube was withdrawn and thoroughly rinsed with water and then dried. As part of the feasibility study, this crystal formation step was repeated up to 3 times to study the degree of crystal embedding/coverage. Thus 3 samples were generated for each membrane pore size.

Results

1. Evidently the hydrotalcite crystal was formed within the porous structure of the $\alpha\text{-Al}_2\text{O}_3$ substrate based upon (i) the significant reduction in permeance of He and N_2 as shown in Table 1, (ii) the increase in the selectivity of He/ N_2 (Table 1), and (iii) the reduction in the pore size and/or pore volume (Figure 9 of Ref. 4). As expected, the pore size reduction for the $0.2\mu\text{m}$ membrane was substantial, specifically, from $0.2\mu\text{m}$ to 0.15, 0.08, and $0.05\mu\text{m}$ for the 1st, 2nd, and 3rd deposition cycles, respectively. The increase in selectivity and reduction in the permeance are supportive of the pore size reduction by the in-situ formation of the hydrotalcite crystal.
2. SEM photomicrographs of the inner and outer tubular surface of the $0.2\mu\text{m}$ membrane after in-situ crystal formation are presented in Figure 1 of Ref. 4. Clearly, no plugging of the inner surface of the membrane was observed. The pore plugging was clearly shown in the outer tubular surface under both low (Figure 1 of Ref. 4) and high magnification (Figure 2 of Ref. 4). EDX mapping shown in Figure 3 of Ref. 4 confirms the formation of the hydrotalcite crystals.
3. The penetration of the crystal is believed to be very limited, since the microporous structure of the cross section of the membrane did not exhibit any deposition even near the outer tubular surface (see Figure 2 of Ref. 4). On the other hand, crystal spill-over to the top of the outer tubular surface is believed to be minimal because the surface topography of the substrate is still visible as indicated by the absence of Mg in these areas (see Figure 4 of Ref. 4). Thus, the morphological evidence indicates that the proposed synthesis protocol delivers an ultrathin hydrotalcite patch within the pores very near the surface of the substrate with little or no excess crystal formation on the surface via the proposed synthesis protocol.
4. A similar result was obtained with the 500\AA substrate shown in Figure 5 of Ref. 4. The pore size reduction in this case was not as obvious as that for the $0.2\mu\text{m}$ substrate; however, it is obvious that the pore volume is reduced

dramatically by the crystals because of the large reduction in gas permeability of the membrane shown in Table 1.

5. Repeated additional depositions of the hydrotalcite crystals further reduced the permeance and pore size. It is believed that the additional depositions resulted in further infiltration of the residual pore openings that remained due to incomplete or non-uniform coverage from previous depositions. However, the majority of the crystals were embedded in the substrate during the 1st deposition cycle based upon the dramatic permeance reduction after the first cycle.

Implications

1. The crystals are clearly embedded within the openings of the porous structure of the substrate. The residual pore volume with pore sizes in the range of $<20\text{\AA}$ to ca. 500\AA is small enough that it can be backpatched using our CVI technique (see Sec. 2).

2. Optimization of the two phase contactor technique is highly recommended during the project study. In addition a continuous 2-phase contactor should be explored as an alternative. Using this method, crystal growth can be made to occur continuously via the supply of fresh reagents to the surface of the substrate. The batch process used in this project does not allow this flexibility. A continuous growth regime is expected to minimize the residual pore volume and pore size, so that a high quality membrane can be prepared.

2. Backpatching with the Chemical Vapor Infiltration (CVI) Technique

Rationale/Justification

1. To avoid non-selective transport through the voids between the single crystals and the base substrate, a chemical vapor infiltration (CVI) technique was proposed. The method has been developed and used by us in the development of our hydrogen selective membranes (SiO₂ and SiC based) [1,2]. The technique has been shown by us to be uniquely suited to the delivery of the precursor within the porous structure at a depth of 1 to 3 μm from the top surface of the substrate (instead of forming an additional layer on the top of the substrate). This unique capability is critical to the hydrotalcite membrane development. Deposition of an additional layer via CVI on the top of the membrane is not acceptable. Such deposition would indiscriminately cover and hence plug the CO₂ transport channels yielding significant reduction in CO₂ permeance and selectivity. Instead, it is necessary to plug only the inter-crystalline void spaces.

Experiment

1. To prove the technical feasibility during this project effort, M&P's existing CVI technique was employed without modifications in the precursor selection and deposition condition. The precursor used is TEOS, the deposition condition is 300°C. At this temperature, the TGA data obtained previously shows that part of the CO₂ transport channels are opened. However, the TEOS precursor molecule is too large to penetrate these openings in the range of 3 to 6 Å. In the feasibility tests, the CVI process was stopped when the reduction in He/O₂ carrier gas permeance was negligible with time.

Results

1. The CVI technique was demonstrated to reduce the residual pore openings of the membrane that remained following the in-situ crystallization discussed in Sec. 1. Table 2 shows that the permeance of a hydrotalcite membrane was reduced from 1.36 to 0.37 m³/m²/hr/bar at 300°C, indicating that the selected CVI condition is sufficient to plug the residual pore openings following in-situ hydrotalcite crystallization.

2. SEM/EDX analysis of a 500 Å substrate following CVI shows that the silicon oxide deposition does not increase the layer thickness of the substrate membrane as evidenced by the grain structure of the top surface of the substrate shown in Figure 6 of Ref. 4. On the other hand, the EDX analysis shows that significant silicon deposition occurs in the first several microns inside the outer surface of the substrate. Thus, it is believed that the CVD technique employed here satisfies our performance requirement, specifically, penetration and plugging of the pore openings without indiscriminant deposition of an overlayer on the top of the existing substrate.

Recommendations

1. CVI of TEOS appears to be very promising. In this project, we will focus on the optimization of the CVI temperature, precursor vaporizer temperature, and the precursor. An ideal CVI temperature would be ca. 250°C at which none of the CO₂ transport channels are open. The 300°C deposition temperature selected in this project matched the conditions used in our in-house development of our core SiO₂-based ceramic hydrogen selective membrane technology. However, it is expected that these conditions are neither ideal nor optimized for the proposed hydrotalcite membrane. Also, to achieve the desired deposition conditions, it may be necessary to alter the precursor. Furthermore, the addition of additives that form pyroceram materials on low temperature calcination [3] could be used to cement the crystals to the pore walls of the substrate.

3. Performance Characterization of Hydrotalcite Membranes

Rationale/Justification

1. Although the unique affinity to CO₂ of the hydrotalcite material has been well established in the literature, it was necessary that we confirm this affinity in the context of a membrane during this project to demonstrate the technical feasibility.

Experimental

1. Permeances of single components, including He, N₂ and CO₂, were measured at 300, 400 and 500°C to determine whether the membrane showed any affinity to CO₂. In our TEOS CVI based hydrogen (and helium) selective membranes, the permeance of N₂ (and CO₂) strictly results from Knudsen flow through defects in the SiO₂ infiltrated layer. Hence, a CO₂ permeance above that expected from Knudsen flow through the defects (which can be estimated from the N₂ permeance) must result from selective transport of CO₂ through the hydrotalcite crystals in the membrane.

2. Enhancement of the CO₂ transport by the hydrotalcite material will peak between 300 and 400°C according to the TGA study of this hydrotalcite material. The enhancement will diminish to negligible levels as the temperature is increased much beyond 400°C, since the hydrotalcite material begins to undergo phase change to a mixed oxide at these temperatures.

Results

1. At 300°C, the CO₂ permeance doubled as a result of the enhancement by the hydrotalcite embedded in the pores as shown in Table 3. The total CO₂ permeance was 0.26 m³/m²/hr/bar. It is estimated that the contribution to the CO₂ permeance from defects in the membrane is 0.14 m³/m²/hr/bar based upon the measured nitrogen permeance and the Knudsen selectivity. Thus, 0.12 m³/m²/hr/bar is the contribution to the CO₂ permeance due to transport of CO₂ through the CO₂ channels in the hydrotalcite crystals.

2. The enhancement at 400°C is reduced to 0.02 m³/m²/hr/bar using a similar analysis as above. The enhancement is expected to be reduced under this experimental condition, since the low partial pressure of CO₂ does not promote adsorption of the CO₂ molecule at this temperature level. In addition, most of the hydroxyl groups available for forming CO₂ via the carbonate ion may be lost so that the injection of water is also likely to be necessary to promote CO₂ permeance enhancement (more discussion in Sec. 4).

Implications

1. Significant CO₂ permeance enhancement attributed to the active transport capabilities of the hydrotalcite material has been demonstrated experimentally. In addition, this enhancement decreases with increasing temperature, consistent with theoretical predictions at this experimental condition. During this project, membrane defects will be further reduced through the optimization of the CVI and in-situ crystallization techniques. In addition, an experimental set-up allowing us to perform the permeance in the presence of water at temperatures up to 500°C and pressures up to 100 psi will be pursued in this project. Thus the full benefit of the CO₂ enhanced transport can be quantified.

4. Experimental Verification of CO₂ Reversibility and Hydrothermal Stability of Hydrotalcite Material

Both CO₂ reversibility and hydrothermal stability of the hydrotalcite material can be confirmed through the performance test of the membrane. However, during the six month this project study, a hydrotalcite membrane was not developed in time for this test. Instead, we have conducted a parallel program using the bulk hydrotalcite material to verify these properties.

Rational/Justification

1. As a viable membrane material, CO₂ affinity should be reversible at the operating condition. Thus, CO₂ can be transported through the membrane based upon the pressure difference between the feed and permeate side. Although literature study indicates the structure reversibility of hydrotalcites [4,5], quantitative information on the degree of reversibility of CO₂ adsorption/desorption at a given temperature and CO₂ pressure is not available. Information like this is essential to develop an optimum operating condition for a given selection of hydrotalcite composition. Thus, a membrane with a tunable separation characteristics becomes feasible.

2. One of the unique features of the proposed hydrotalcite membrane is its excellent hydrothermal stability as discussed previously based upon the material structure and its transport mechanism. However, an experimental study demonstrates that the ability to transport CO₂ in the presence of steam would be essential to prove the intrinsic hydrothermal stability of hydrotalcites at a given condition.

Experimental

1. Hydrotalcite (prepared in this project) was thermally treated at a high temperature, i.e., 350°C to remove a majority of adsorbed carbonate species. Then, the hydrotalcite was exposed to a stream of water and CO₂ at various pressures to determine the degree of carbonate ions to be recovered. DRIFTS was used to monitor on-line the pick-up of carbonate and water on the surface of hydrotalcites. This study provides qualitative evaluation on the CO₂ reversibility and the role of water for the active CO₂ transport.

2. In addition, TGA was used to determine weight gain of the thermally treated material after exposed to CO₂. Unfortunately the TGA set-up does not allow the operation pressure exceeding 1 atmosphere. This has limited our reversibility study.

Results

1. Significant pick-up of OH⁻ and CO₃²⁻ was observed for hydrotalcite after exposed to equimolar CO₂ and water mixture at 4 bar and 250°C. Figure 7 of Ref. 4 generated from the DRIFTS study shows a substantial absorption of OH⁻ group represented by 3470cm⁻¹ and CO₃²⁻ represented by 1540 and 1438 cm⁻¹. According to the literature, the weight loss vs. temperature of the hydrotalcite materials is resulted from the composition change as follows:

Thus the significant absorption of OH⁻ and CO₃²⁻ observed in Figure 7 of Ref. 4 is consistent with the composition change postulated in the literature [4]. Our ability to reabsorb CO₂ back to the hydrotalcite in the presence of a high pressure steam verifies the reversibility of the CO₂ affinity and its intrinsic hydrothermal stability. Additional study is continuing to obtain a complete reabsorption profile for a wide range of pressure and temperature.

2. The TGA study shown in Figure 8 of Ref. 4 indicates the weight pick-up of ~1 wt% during the reabsorption of humidified CO₂ at an ambient pressure and 350°C. Although this level of weight gain is much lower than the total weight loss from the TGA study reported in the 1st quarterly report, it may be adequate for a steady state transport of membrane. A significant weight gain is expected at a higher pressure as shown above.

Implications

1. The significant reabsorption of carbonate ions at 250 to 350°C on the thermally treated material indicates that the CO₂ affinity of the hydrotalcite material can be reversible at a high temperature environment. In addition, the ability of reabsorbed CO₂ in the presence of water (2 bar) indicates the hydrotalcite material is most likely hydrothermally stable at least from the CO₂ transport standpoint. More quantitative information will be generated in this project using the methodology developed here as a qualitative tool as well as the traditional adsorption technique which allows us to generate information at a higher pressure environment required by a membrane operation.

REFERENCES CITED

1. Wu., J.C.S., Sabol, H.K., Smith, O.W., Flowers, D.F., Liu, P.K.T., J. Membrane Science, 96, 275 (1994).
2. Liu, P.K.T., and Wu, J.C.S., U.S. Patent 5,415,891, May 16(1995).
3. Corning Ceramic Bulletin on Pyroceram.
4. Due to the large datadile, all figures are not included in this report. However, these figures can be requested directly from Media and Process Technology Inc. via the e-mail (mandpmain@aol.com).

Table 1: Permeance and Selectivity of the 500Å and 0.2µm Pore Size Ceramic Substrates Following In-situ Deposition/Crystal Growth of Hydrotalcite within the Pores. Based Upon the SEM Analysis, Crystal Growth is Concentrated at the Surface of the Membrane.

Pore Size of Substrate [µm]	Times of Deposition [-]	Permeance [m ³ /m ² /hr/bar] @ 25°C		Ideal Selectivity [-]	Remarks
		Helium	Nitrogen		
0.05	0	81.2	41.5	1.96	control
0.05	1	2.04	0.913	2.24	
0.05	2	-	-	-	
0.05	3	5.22	2.35	2.22	
0.2	0	113	66.3	1.70	control
0.2	1	18.8	11.2	1.68	
0.2	2	-	-	-	
0.2	3	15.0	6.52	2.30	

Table 2: Chemical Vapor Infiltration as a Backpatch for Hydrotalcite Membranes

Samples	Temperature [°C]	Helium Permeance [m ³ /m ² /hr/bar]	Nitrogen Permeance [m ³ /m ² /hr/bar]	Experimental He/N ₂ Selectivity	Theoretical He/N ₂ Selectivity
Before CVD	300	1.36	0.59	2.32	2.65

After CVD	300	0.37	0.16	2.23	2.65
-----------	-----	------	------	------	------

Table 3 Chemical Vapor Infiltration as a Backpatch for the Hydrotalcite Membrane. The Improvement in CO₂ Permeance due to Active Transport is shown at Various. The CO₂ Permeance in the Defects is Determined Using the Nitrogen Permeance and the Knudsen Selectivity. Permeance is in m³/m²/hr/bar.

	Temp [°C]	Pres [psi]	He Perm	N ₂ Perm	CO ₂ Perm	CO ₂ Permeance due to Defects	<i>CO₂ Permeance due to Enhanced Transport</i>
Before CVD	300		1.36	0.59	-	-	-
After CVD	300		0.37	0.16	-	-	-
Post-CVD	300	15	0.36	0.17	0.26	0.14	<i>0.13</i>
Post-CVD	400	15	0.46	0.19	0.17	0.15	<i>0.02</i>
Post-CVD	500	15	0.84	0.36	0.29	0.29	<i>0.00</i>